OUTGASSING PRODUCTS FROM ORBITER TPS MATERIALS

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ABSTRACT

The Space Transportation System (STS) orbiters are known to be significant sources of outgassing in low earth orbit (LEO). Infrared and mass spectra of residues and outgassing from orbiter thermal protection tile and an external blanket are presented. Several sources of methyl and phenyl methyl silicones are identified. About fifty pounds of silicones are estimated to be outgassed during an STS mission.

INTRODUCTION

On-orbit contamination of the payload bay was reported for the early shuttle flights (Ref. 1). Several of these measurements showed more than 5 mg/0.1m^2 (5 mg/ft^2) molecular depositions and it was concluded that, "some sensitive experiments would require protective action." Later, many experimenters identified silica films or silicon-rich films on LDEF surfaces and experiments. References 2-9 are a partial list of early reports of atomic silicon or silica (SiO_2) by surface analyses. Reference 10 reports multiple laboratory analyses of the Z306 black paint and primer, used on the LDEF, which show no silicones in the paint or primer. Reference 11 reports that the films on the space exposed surfaces of optical windows in Tray E5 were primarily silica. Reference 11 also reports silicone outgassing in the Payload Changeout Room (PCR) at Kennedy Space Center (KSC). Reference 12 reports silicone residues (chemical reaction products) from the orbiter rewaterproofing compounds and chemical reversion of the Thermal Protection System (TPS) adhesive, RTV 560, caused by the rewaterproofing compound, hexamethyldisilizane (HMDS), Ref.13, used for the LDEF deployment mission. The outgassing of silicones from Atlantis was measured on STS 44 (Ref. 14) and is probably a major source of silicone contamination (up to 26 mg/0.1m^2) seen on attached instruments flown on Atlantis during STS 45 and 46 (Ref. 15). The silicon contamination on attached instruments was reported at two Technical Interchange Meetings (November 1992, Johnson Space Center (JSC) and August 1993, KSC) on STS Payload Contamination.

This paper reports significant outgassing of TPS tile and external flexible insulation blanket (FIB) from the Columbia, at ambient (unheated) temperatures. These outgassing tests indicate that tens of pounds of phenyl methyl silicones are outgassed by the orbiters in LEO during a typical STS mission.
Most STS payloads are not adversely affected by this outgassing. However, understanding of the orbiters' outgassing environment is needed for instrument and spacecraft designers and mission operators to minimize contamination of sensitive instruments. High spectral stability optical instruments, low friction mechanical devices, micrometeoroid chemical analyses experiments, and thin film materials are examples of possible contamination sensitive experiments.

CLEANLINESS MEASUREMENTS OF ATLANTIS AND COLUMBIA

Most of the surface chemistry analyses of LDEF which revealed silica films were performed with scanning electron microscopes (Refs. 3-5). However, the silica films can also be detected on suitable substrates by the 10-micron SiO absorption in the infrared spectrum (Ref. 11). A calcium fluoride optical window was flown on STS 46 and the pre- and post-flight IR spectra are shown in Figure 1. The SiO_2 thin glass film absorption is the only contamination indicated by IR spectroscopy. This spectrum and surface analysis of a quartz crystal microbalance housing flown on the same flight indicate quick and nearly complete conversion of silicone contamination to glass films by solar ultraviolet and/or atomic oxygen.

Cleanliness wipes of the orbiter Columbia using twice Soxhlet extracted polyester wipes and analytical grade isopropyl alcohol were performed November 17, 1992. Six wipes were taken in the payload bay and showed about one milligram/0.1m^2 of mostly esters (Table 1). One wipe (#7) of an external FIB

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about midway along the fuselage gave 0.35 mg/.1m^2 of NVR that was mostly methyl silicone (Figure 2). These measurements indicate that most of the silicone outgassing of the orbiters is from external surfaces.

Similar wipes reported by a KSC group at the second technical interchange meeting (TIM) on STS payload contamination showed the payload bays of Columbia, Discovery, and Endeavor to generally have less than one mg/0.1m^2 of molecular films and these films were not silicones.

TRANSPORT MECHANISM OF ORBITER OUTGASSING

The long ambient mean-free-path in LEO (~ 2km at 300km altitude, Ref. 16) was cited at the first TIM on STS payload contamination as a reason that outgassing from external orbiter surfaces could not return to the payload bay. In other words, it was alleged there was no transport mechanism for return flux of outgassing from the orbiter. However, Reference 17 reported on-orbit pressures of 10^{-5} to 10^{-6} Torr which correlate to mean-free-paths of 25 to 700 cm (Ref. 16). Reference 18 reports on-orbit pressures in the payload bay for early STS missions of 4.4×10^{-4} Torr (mean-free-path ~12 cm) to 8.3×10^{-6} Torr (mean-free-path ~620 cm). The microatmosphere (orbiter glow) around an orbiter has been photographed (Ref. 19). The microatmosphere is mostly outgassing H_2O, N_2, and O_2 from adsorbed surfaces and trapped volumes of the orbiter. Thus, there is a transport mechanism for return flux on STS missions.

TPS MATERIALS AND CLEANLINESS

The rewaterproofing compounds immediately react with water to produce silanols which then react to form silicones which can outgas later (Ref. 11). However, other silicon based materials are also used in the orbiter's thermal protection system (Table 2). RTV 577 is a calcium oxide filled (white) phenyl methyl silicone used as a screed or filler between the orbiter body and the TPS. RTV 560 is an iron oxide filled (red) phenyl methyl silicone with high heat conductivity that is used as the TPS adhesive (Ref. 12). The black RTV is a methyl silicone used as gasket material on doors and hatches. The amount of RTV 560/orbiter was calculated by weighing 1 inch square of adhesive from the back of a damaged tile, and an FIB and multiplying by the TPS surface area (1200 m^2) of the orbiter (Ref. 12). A similar mass was estimated from visual inspection for the RTV 577. The amount of black RTV was obtained from the material replacement log for an orbiter refurbishment.

A 1/2 inch cubed section from the back of a 0.025m^2 TPS tile (Fig. 3) was extracted by soaking in analytical grade isopropyl alcohol for 30 minutes. The infrared spectrum of the residue (Fig. 4) is that of phenyl methyl silicone and is identical to that from RTV 560. A similar size section from the interior or core of a tile was also extracted. The infrared spectrum of residue from the core of a tile (Fig. 5) shows the same phenyl methyl silicone and indicates that outgassing from the RTV 560 is absorbed within the tile. A similar amount of debris (0.5 in^3) from an FIB (Fig. 6) removed from Columbia in September 1992 also had phenyl methyl silicone NVR (Fig. 7). However, the non-volatile residue (NVR) from a TPS gap filler was mostly esters .

The TPS tile (Fig. 3) was placed in a high-vacuum chamber (~10^{-7} Torr) and the outgassing at ambient temperature was measured with a mass spectrometer. The chamber background spectrum and the tile outgassing spectrum are shown in Figure 8. The heavy mass fragments are listed in Table 3 and show that the outgassing is phenyl methyl silicone. The absence of mass fragments 147 and 149 shows that the outgassing is not methyl silicone, or alkyl phthalates (the most common NVR on LaRC flight hardware). Similar outgassing measurements of TPS tile (Ref. 20) at Marshal Space Flight Center (MSFC) in 1975 also showed about one gram/0.1m^2 of phenyl methyl silicones.

The FIB from Columbia (Fig. 6) was placed in the same high-vacuum chamber and exposed to high vacuum at ambient temperature (27°C) for 3 days. The mass spectrum of outgassing from the FIB (Fig. 9) is identical to that from the TPS tile. More than 1- 1/2 grams of clear fluid was collected on the scavenger plate maintained at -100°C during this test. This corresponds to about 20 lbs of phenyl methyl silicone outgassing from an orbiter over 3 days in LEO, or an estimated 50 lbs of silicone outgassing over a 9- to 12- day mission. An IR spectrum of the clear fluid is presented as Figure 10. A similar test of a 0.4 m^2 beta cloth/multilayer insulation blanket flown on EURECA showed no silicone outgassing. Similar outgassing measurements of felt reusable surface insulation (FRSI), Ref. 20, at JSC in 1976 also showed about one gram/0.1m^2 of residue.

Another type of evidence of outgassing of TPS materials is shown in Figures 11 and 12, photographs of black ceramic TPS tiles taken immediately after mission STS-49, the maiden flight of the Endeavor. Figure 11 is a closeup photograph of discolored tiles aft of the nose landing gear door, and Figure 12 is a photograph of heavy outgassing deposits on the elevon leading edge. In most cases the white color results from diffuse scattering of light from glassy deposits. The entire tile surface (black and white, Fig. 5) appears, under a 80X microscope, to be coated with a thin transparent film. Some of the white areas are pits which are partially filled in. The heavy white streams are multiple crazed and fused layers of relatively thick glass deposits. The black ceramic tile are good optical witness plates because of the high contrast and the flat surfaces which aid microscope examination.

A small data base of flight hardware cleanliness measurements has contributed to much confusion in the past regarding outgassing from the orbiters.

Several groups have been extremely helpful to the present study of outgassing of the orbiters. This work would not have been possible without their professional integrity and technical competence. We wish to acknowledge especially Jaime Palou and Frank Jones for their essential contributions.

CONCLUSIONS

Outgassing of large amounts of silicones by the orbiters has been confirmed by several independent measurement techniques (spacecraft and attached instrument glass films and silicone residues, surface wipes, IPA extraction of TPS materials, vacuum outgassing of TPS tile and blanket, and photographs of glassy deposits on TPS tiles). The LDEF and many shuttle attached instruments have experienced depositions of silicones which were converted to glass in LEO. The ubiquitous nature of these silicone-to-glass films strongly indicated sources within the orbiters. Several orbiters' TPS materials have been shown to significantly outgas silicones in LEO. In particular, vacuum outgassing measurements show the TPS adhesive, RTV 560, and the screed filler, RTV 577, can be expected to outgas about 50 lbs of silicones during a typical mission. There was probably even more outgassing of silicones from the Challenger during deployment of LDEF (STS-41C) due to the wide spread reaction with hexamethyldisilizane, the TPS rewaterproofing compound used for that mission.

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TABLE 1 - CLEANLINESS WIPES OF COLUMBIA (11/17/92)

Wipe #	Location	Evaporation dish	Weighing pan
1	Port sill X775.5	Much fluid and particles	Mostly fluid
2	Sill near monkey fur seal	Some particles, a little fluid	Unmixed fluids
3	PL support equip, B5	Much fluid	Much fluid, fibers
4	PS, B5 cable tray	Mostly particles, some fibers	Fluid, fibers,
5	PS, B5/6, cable tray	Mostly particles, gel	Mostly fluid
6	Avionics shelf, B5	Fluid, fibers, particles	Fluid, fibers, particles
7	Port fwd BLBD exterior	Mostly dust (fine particles)	Mostly particles

Wipe #	Recovered mass(mg)	IR	Comments
1	0.79	Mostly esters	6" x 6" wipe of sill
2	0.17	90% fluorocarbons (Braycote)	
3	2.78	~ 70% HC, 25% CH_3SiO	
4	1.01	Mostly esters	
5	0.62	CH_3SiO and esters	
6	1.11	Mostly esters	
7	0.35	90% CH_3SiO	

TABLE 2-ORBITER TPS SILANES

Compound	~Amount
DMES-dimethylethoxy silane	200 lbs/mission
RTV 560 (red RTV)	1200 lbs
MTMOS-methyltrimethoxy silane	
TEOS-tetraethyl orthosilicate	10 lbs
LUDOX-colloidal silica	2 lbs/mission
MBO 124-085(Scotchguard)	2 lbs
Black RTV	10 lbs/mission
RTV 577 (white RTV)	1200 lbs

TABLE 3 - MASS FRAGMENTS FROM TPS TILE

AMU	Mass Fragments Present
73	$(CH_3)_3Si^+$
78	C_6H6^+
135	$(CH3)_2C_6H_5Si^+$
197	$(CH_3)(C_6H_5)_2Si^+$
	Mass Fragments Missing
147	$(CH_3)_3SiO(CH_3)_2Si^+$
149	alkyl phthalates

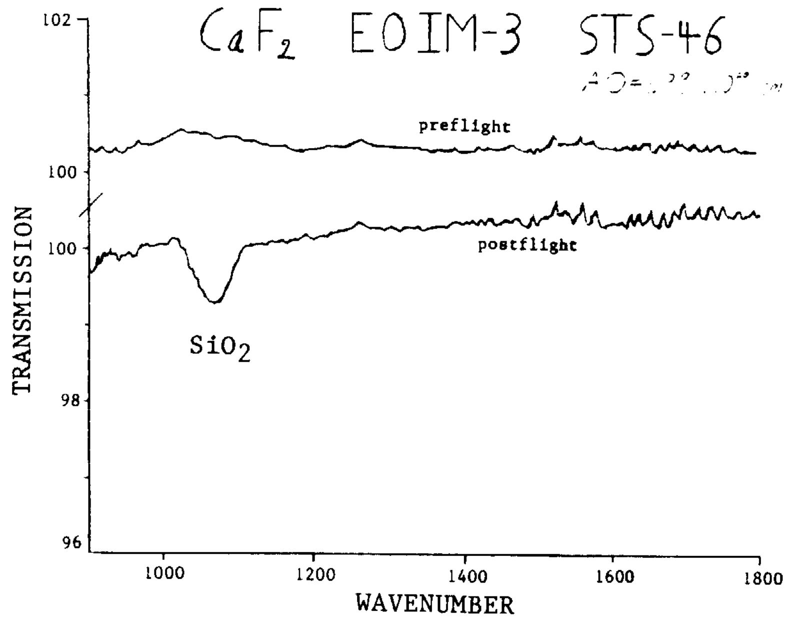

Figure 1. IR spectrum of SiO_2 on CaF_2 window flown on STS-46.

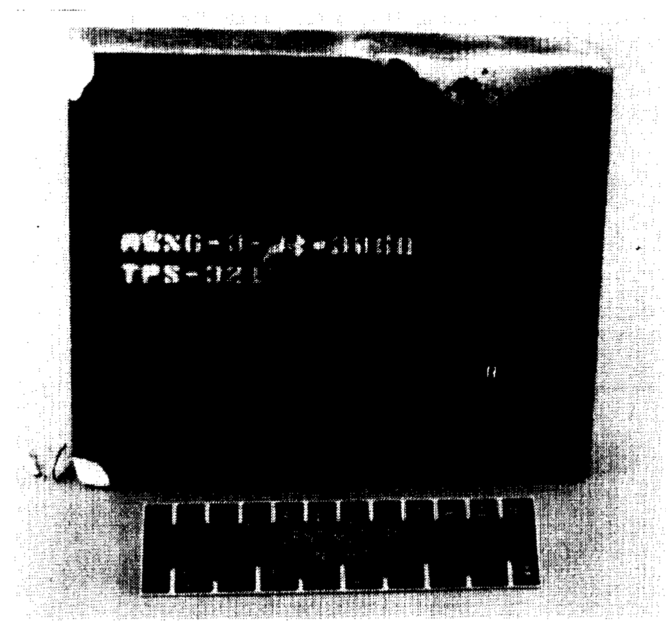

Figure 3. Photograph of a TPS tile.

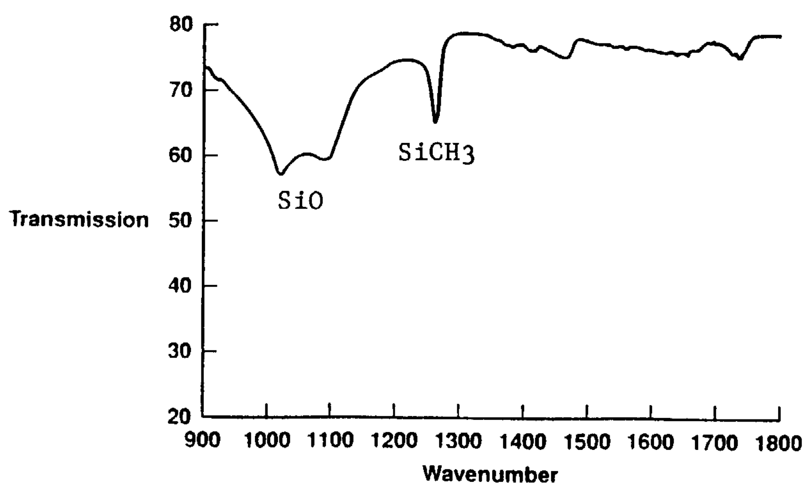

Figure 2. IR spectrum of NVR from Columbia FIB.

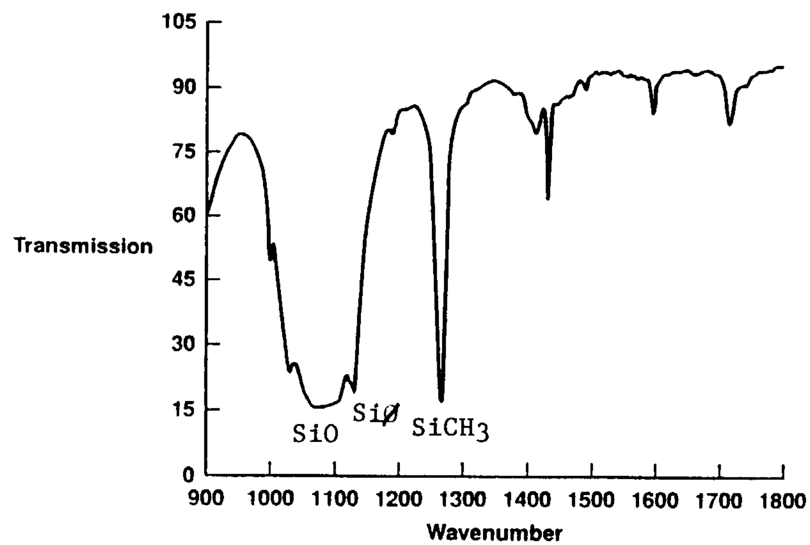

Figure 4. IR spectrum of NVR from back of TPS tile.

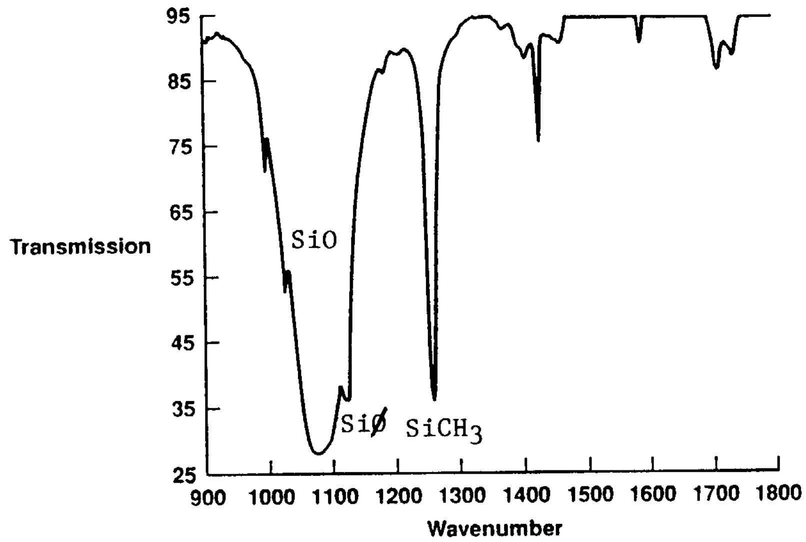

Figure 5. IR spectrum of NVR from core of TPS tile.

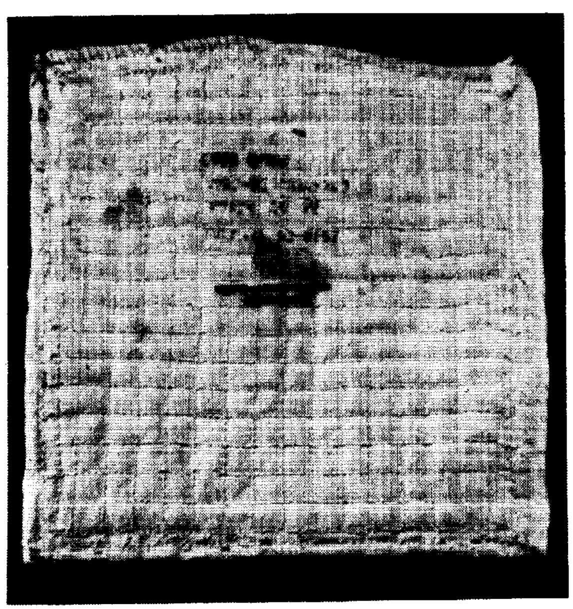

Figure 6. Photograph of FI blanket from Columbia.

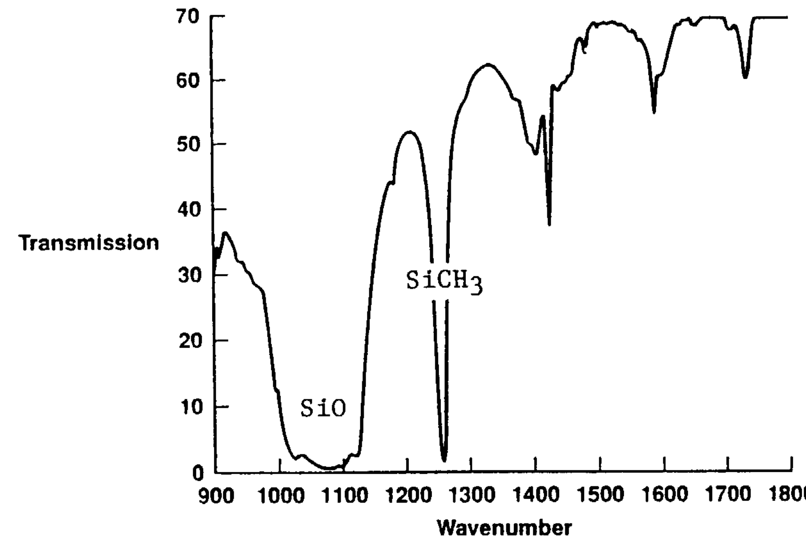

Figure 7. IR spectrum of NVR from FIB debris.

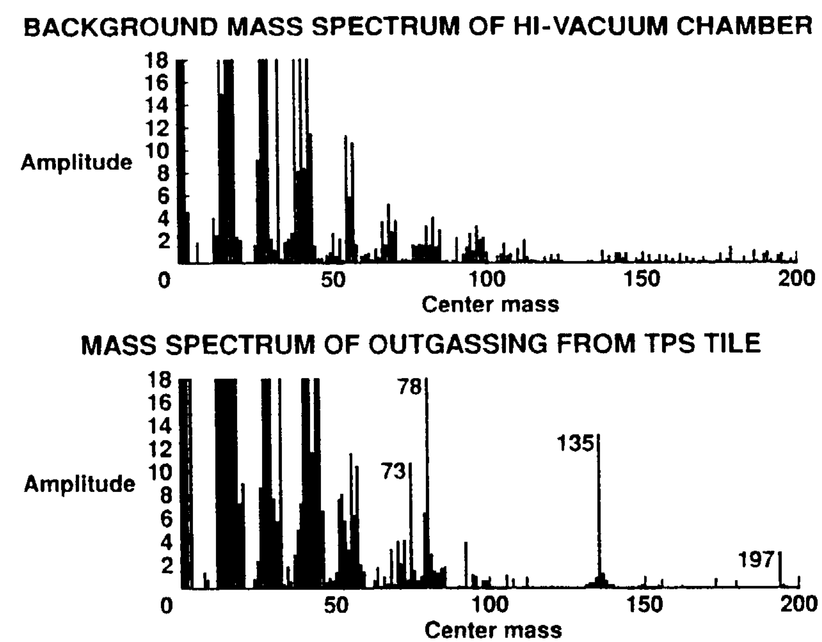

Figure 8. Mass spectrum of outgassing from TPS tile.

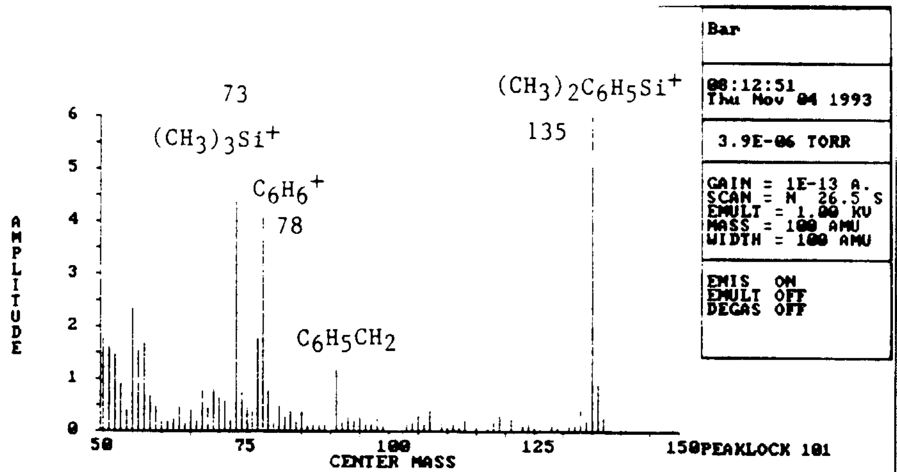

Figure 9. Mass spectrum of outgassing from Columbia FIB.

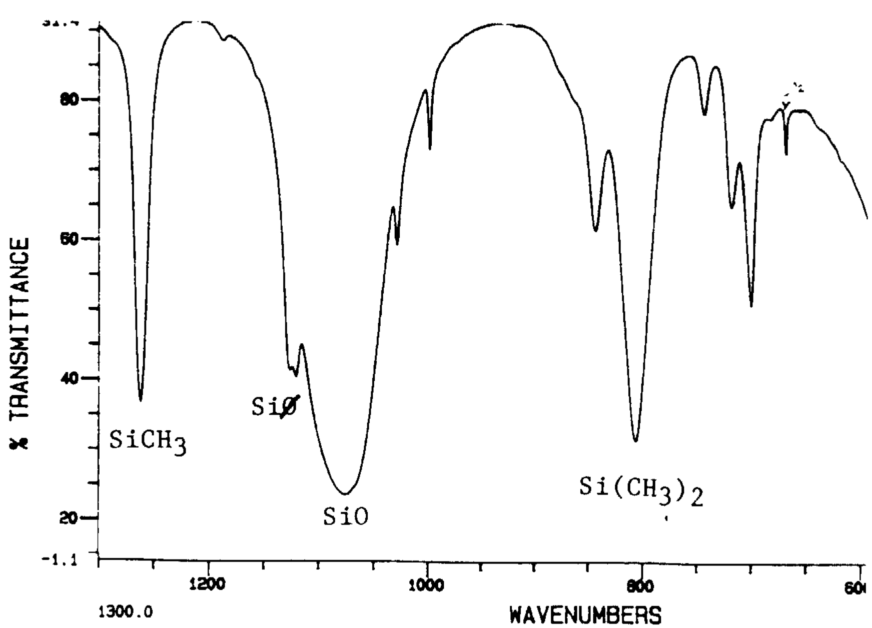

Figure 10. IR spectrum of trapped NVR from Columbia FIB.

Figure 11. Discolored tile aft of Endeavor Landing Gear door (May 1992).

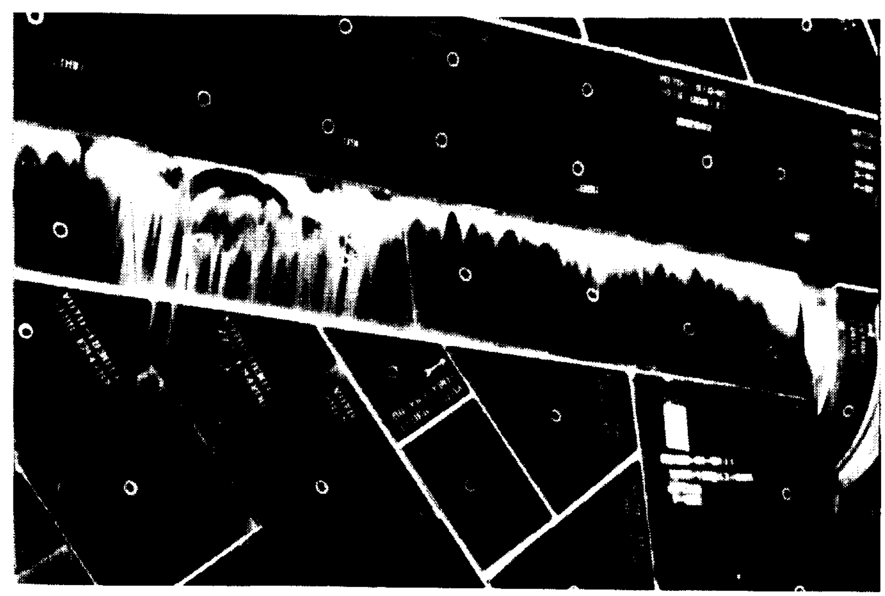

Figure 12. Heavy outgassing deposits on the elevon leading edge of Endeavor (May 1992).

EUROPEAN RETRIEVABLE CARRIER (EURECA)